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Nielsen, Sanne Skov

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Address: DTU Environment
Department of Environmental Engineering
Technical University of Denmark
Miljoevej, building 113
2800 Kgs. Lyngby
Denmark

Phone reception: +45 4525 1600
Fax: +45 4593 2850

Homepage: http://www.env.dtu.dk
E-mail: reception@env.dtu.dk

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Preface

This thesis presents the outcome of a PhD study conducted at Department of Environmental Engineering, Technical University of Denmark. The project was supervised by Associate Professor Rasmus Jakobsen (primary supervisor) and Professor Peter Kjeldsen (co-supervisor). The PhD was carried out as part of the project Innovative REMediation and assessment TEChnologies for contaminated soil and groundwater (REMTEC) and was primarily funded by the Strategic Research Committee and the Technical University of Denmark.

The following three scientific journal papers, of which one is published and two submitted to scientific journals, are part of the thesis:

I. Nielsen, S. S., L. R. Pedersen, P. Kjeldsen and R. Jakobsen (2011): **Amendment of arsenic and chromium polluted soil from wood preservation by iron residues from water treatment.** Chemosphere 84(4) 383-389.

II. Nielsen, S. S., P. Kjeldsen, and R. Jakobsen**: Field scale amendment of a wood impregnation site using iron water treatment residues.** Manuscript submitted to Journal of Soils and Sediments.

III. Nielsen, S. S., P. Kjeldsen, H. C. B. Hansen and R. Jakobsen**: Transformation of natural ferrihydrite aged in As, Cr and Cu contaminated soil studied by reduction kinetics**. Manuscript submitted to Applied Geochemistry.

In the thesis these papers are cited by their roman numerals e.g. Nielsen et al. (I).

In this online version of the thesis, the papers are not included but can be obtained from electronic article databases e.g. via www.orbit.dtu.dk or on request from: DTU Environment, Technical University of Denmark, Miljoevej, Building 113, 2800 Kgs. Lyngby, Denmark, reception@env.dtu.dk.

Kgs. Lyngby, June 2013
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My involvement in the Collstrop sites was initiated by the report done at request of John Flyvbjerg and Kim Sørensen from the Capital Region of Denmark, who also provided financial assistance for some of the initial field work and access to the site. As site owner Naturstyrelsen represented by forest manager Hans Holbech gave kind permission to the field work. Soil mixing was done by Arkil A/S, with Kim R. Jensen as project manager and the excavator elegantly operated by Tommy Solberg. Ib Ambrosiusen from Nordvand A/S supplied the iron water treatment residues from Sjælsø Waterworks.

In the finishing stages of my Ph.D. work Thomas Hauerberg Larsen came to rescue with all of his skills and kind sympathy. He and my colleagues at Orbicon made the final push bearable and work has never been as fun as in 364.

Coffee, Scrabble and beer breaks were provided by my officemates: Ida, Timo, Julie and Nanna and from other offices: Claire, Claus, Niels, Silvio and Julie. Our daily meetings in the Butter Club will be what I miss the most from my time in DTU and for a long time to come my stomach will remind of you guys every day at 10.00. No longer officially in DTU but still around, Chiara, Claire and Ida had the tedious task of correcting my writing. Thank you so much!

Many rock, plastic and tree climbers and all the marvelous people I know through FDF helped taking my mind off work. I look forward for our adventures to come. And finally thank you for love and support to Gitte, Mor and Far

Summary

Chromated Copper Arsenate (CCA) is a mixture of arsenic, chromium and copper salts which have widely been used for impregnation of wood. World-wide many contaminated sites and brownfields exist, where wood impregnation with CCA has taken place, resulting in soil contamination and leaching of contaminants. Arsenic, chromium and copper cannot be degraded and existing methods for cleaning the soil are rarely used as they are expensive and technically demanding.

Chemical stabilization of polluted soil is an alternative method for soil remediation, especially metal contamination, and consists in adding an amendment to immobilize the contaminants. Cement is often used, because it, in addition to chemical stabilization, also improves the geotechnical strength as well as reducing hydraulic conductivity, but the stabilization can be purely chemical and done by amending the soil with iron containing substances or other sorbents. Iron water treatment residues mainly consist of ferrihydrite, an oxidized iron oxy-hydroxide with a high reactivity and a large specific surface area with a high capacity for adsorption. Iron water treatment residues (Fe-WTR) are a by-product from treatment of groundwater to drinking water and can be used as a soil amendment to decrease the mobility of CCA in contaminated soil.

Stabilization with Fe-WTR was tested at the Collstrop site in Hillerød, Denmark. The site has been polluted with a wide range of wood impregnation agents including CCA during 40 years of wood impregnating activities at the site. Since activities ceased at the site more than 30 years ago it has been a brownfield with ongoing monitoring of arsenic contaminated groundwater. The first 1 m^2 small-scale field experiment was amended with 2.5% Fe-WTR and monitored for 3 consecutive years, during which the amendment showed a remarkable effect on the porewater. Porewater concentrations of arsenic decreased by two orders of magnitude in the amended soil compared to an undisturbed soil profile.

A full scale field experiment was then initiated, where mixing of soil and Fe-WTR was done with an excavator mounted with a rotary screening bucket. In two plots of 100 m^2 soil was homogenized with the screening bucket to 1 meter below ground and one of those plots was simultaneously amended with Fe-WTR. An unexpected high water content of the Fe-WTR made the amendment only 0.6% dry weight of the soil and subsequent analysis of Fe concentrations in the amended soil showed an uneven distribution of the amendment. Analysis of the

porewater from June 2011 to July 2012 showed that arsenic, chromium and copper in porewater was reduced more than 90% in the part of the field that received the most Fe-WTR amendment, even at this low addition ratio.

In a series of batch leaching tests, where polluted soil from the Collstrop site was amended with 5% dry weight Fe-WTR, the leaching of arsenic in strongly polluted soil was decreased by 98% and 91% for chromium compared to unamended soil. The concentration of pollutants in the leachate from an amended, slightly polluted soil (255 mg/kg As and 27 mg/kg Cr) did not at any time exceed 50 µg/L, which means that the soil can be reused for construction e.g. roads and baffle walls as described by the Danish Reuse Act.

Ageing of ferrihydrite, the main constituent of Fe-WTR, is of concern as the retention of contaminants may decrease during its transformation to other iron phases. To study the transformation of ferrihydrite, permeable bags containing fresh Fe-WTR were buried at the field site for 4 years. Reactivity as a measure of the degree of transformation was determined by reduction in 10 mM ascorbate at pH 3. As transformation products are much less reactive, this method can be used to quantitatively determine the transformation and reduction rates which were found to be up to one order of magnitude lower in the aged Fe-WTR compared to fresh Fe-WTR. Oxalate-extractable iron decreased from 95% in fresh samples to 40-50% in the aged samples and transformation products characterized by XRD were primarily goethite. During burial Fe-WTR has scavenged the soil porewater for especially As and Cu, increasing contaminant fractions from trace amount to up to 9.2 mmolAs/molFe and 1.5 mmolCu/molFe. Contaminants were equally associated with the oxalate-extractable iron fraction and the remaining iron fractions, suggesting that sorption capacity does not decrease dramatically with transformation. Increased leaching of contaminants with time was not observed in field experiments as natural variability was too large to for this effect to be observed, but indications of a decrease of As retention was observed after 103 days in the controlled environment of the batch experiment.

Increased porewater concentrations of arsenic were observed in the small-scale experiment during winter, where increased precipitation floods the soil and creates possible iron reducing conditions in the lower parts of the amended plot. In the field scale experiment measurements of the secondary groundwater table proved, that the soil was periodically flooded and iron, but not arsenic, concentrations increased during flooding in the unamended field.

Dansk resumé

Krom, kobber og arsen (CCA) har været anvendt i en række træimprægneringsmidler med det formål at forhindre nedbrydning af træet. Over hele verden findes forurenede lokaliteter og efterladte industrigrunde (brownfields), hvor der er blevet imprægneret træ, og hvor denne aktivitet har medført spild af imprægneringsvæske og dermed forurening of jord og grundvand. Arsen, krom og kobber er grundstoffer og kan derfor ikke nedbrydes, og eksisterende metoder til at rense jorden benyttes sjældent, da de er dyre og teknisk krævende.

Kemisk stabilisering af forurenet jord er et alternativ til jordrensning, især for tungmetaller, og består i at tilføre jorden en sorbent, der kan immobilisere forureningen. Ofte bruges cement, fordi det udover den kemiske stabilisering også nedsætter den hydrauliske konduktivitet, men stabiliseringen kan også være rent kemisk og bestå af jernholdige forbindelser eller andre sorbenter. Okkerslam er et affaldsprodukt fra behandlingen af grundvand til drikkevand, og produceres ved simpel kemisk fældning på vandværkerne. Størstedelen af okkerslammet består af jernoxyhydroxidet ferrihydrit, der har en høj reaktivitet og et stort specifikt overfladeareal med et godt sorptionspotentiale. Dermed kan okkerslammet bruges som sorbent til at reducere udvaskningen af CCA fra forurenet jord.

Stabilisering med okkerslam blev testet på Collstropgrunden i Hillerød. Grunden er forurenet med en lang række træimprægneringsmidler, deriblandt CCA-salte, gennem 40 års produktion af bl.a. telefonpæle. Siden produktionen blev nedlagt og bygningerne fjernet for mere end 30 år siden, har grunden været ubenyttet og afskærmet for offentligheden på grund af omfattende jordforurening, og grundvandsforureningen med arsen moniteres løbende. Et lille feltforsøg på bare 1 m^2, hvor jorden blev behandlet med 2.5% okkerslam og moniteret i 3 år, viste at behandlingen har stor effekt på mobiliteten af arsen. Koncentrationen af arsen i porevandet i det behandlede felt var 2 størrelsesordner mindre end i et uforstyrret og ubehandlet jordprofil ved siden af.

Et fuldskala feltforsøg blev derefter etableret, hvor opblandingen af jord og okkerslam blev udført med en gravemaskine påmonteret en roterskovl. I to forsøgsfelter på hver 100 m^2 blev jorden homogeniseret med roterskovlen ned til 1 meters dybde og det ene felt blev tilsat okkerslam. På grund af et uventet højt vandindhold i okkerslammet blev tilsætningen af okkerslam kun 0.6% tørvægt og

efterfølgende analyse af jernindholdet i det behandlede felt viste, at okkerslammet var ujævnt fordelt i forsøgsfeltet. Indholdet af arsen, krom og kobber i porevandet blev dog reduceret mere end 90% i den del af forsøgsfeltet, der indholdet mest okkerslam, selv med det lave tilsætningsforhold.

I en række udvaskningforsøg, hvor forurenet jord fra Collstropgrunden blev behandlet med 5% tørvægt okkerslam, blev udvaskningen af arsen nedsat med 98% og 91% for krom i den mest forurenede jord forhold til en tilsvarende ubehandlet jord. Koncentrationen af forureningsstoffer i eluatet fra den knap så forurenede jord (255 mg/kg As og 27 mg/kg Cr) overskred på intet tidspunkt 50 µg/L, grænseværdien for jord til genanvendelse i f.eks. veje og støjvolde.

Ferrihydrit, der udgører størstedelen af okkerslammet, er meget reaktivt og vil med tiden rekrystalliseres til andre jernoxider, hvilket formodes at medføre forringet sorptionskapacitet. For at undersøge transformationen af ferrihydrit, blev permeable nylonposer indeholdende nyudfældet okkerslam nedgravet på Collstropgurnden og genopgravet 4 år senere. Reaktiviteten, der bruges som mål for graden af rekrystallisering, blev målt ved reduktiv opløsning i 10 mM ascorbinsyre ved pH 3 på poserned indhold. Da de mineraler, der dannes ved rekrystalliseringen, er mindre reaktive end ferrihydrit, kan denne metode bruges til at måle graden af rekrystallisering. Reduktionsraterne var op mod 1 størrelsesorden mindre end for frisk okkerslam. Mængden af oxalatekstraherbart jern var ligeledes formindsket fra 95% i frisk okkerslam til 40-50% i de devist rekrystalliserede prøver. Under nedgravningen optog okkerslammet især arsen og kobber fra porevandet, hvilket medførte, at indholdet af arsen og kobber i poserne steg fra ubetydelige koncentrationer til op mod 9.2 mmolAs/molFe og 1.5 mmolCu/molFe. Forureningsstofferne var ligeligt fordelt mellem den oxalataekstraherbare fraktion og den mere krystallinske fraktion, hvilket tyder på, at sorptionskapaciteten ikke formindskes dramatisk ved rekrystalliseringen. I feltkesperimenterne med okkerstabilisering blev ikke observeret øget udvaksning med tiden på grund af stor variation i de målte koncentrationer, men i udvaksningsforsøget udført i laboratoriet, var der tendes til øget udvaskning af arsen mod slutningen af de 103 dage forsøget varede.

Om vinteren, når vandspejlet står højt, steg porevandskoncentrationerne af arsen i det lille feltforsøg, formentlig som følge af jernreduktion i den nederste del af forsøgsfeltet. I det store fuldskalaforsøg viste målinger af vandspejlet i det sekundære grundvand, at jorden var periodevis oversvømmet, og jern, men ikke arsen, blev frigivet i det ubehandlede felt.

List of contents

1 Introduction

Former industrial sites, termed brownfields, are of great environmental and socio-economic importance (USEPA, 2006). Many brownfields are situated within urban areas and have negative economic and environmental effects on the surrounding community (USEPA, 2006). Environmental effects are often caused by contamination as many brownfields stem from early industrial development, before environmental protection laws existed (Buzbee, 1997). More than 450,000 brownfields exist in the United States (USEPA, 2006) and over 700,000 brownfields and contaminated sites are found in the EU (Oliver et al. 2005). Contamination in these brownfields is diverse, ranging from almost immobile compounds, which can still cause a threat to human health from dust exposure and ingestion, to more mobile contaminants. The latter may pose a risk by dissolving in percolating rain and may end up in ground water used for drinking water supply or in surface water. In surface waters the compounds can be toxic to organisms at low trophic levels and/or be bio-accumulated through the food chain eventually becoming toxic in the higher trophic levels, including humans. The redevelopment of brownfields therefore often includes contaminant remediation to protect the surrounding environment including ground and surface waters (USEPA, 2005).

For the last couple of decades a focus on cost effective methods for redeveloping these brownfield sites has been set, trying to reduce risk to both humans and the surrounding environment using economically feasible solutions. Many methods focusing on organic contaminants have been developed, because they comprise most of the mobile compounds, e.g. chlorinated solvents and oil products (Lombi and Harmon, 2005). Less attention has been given to metals and metalloids as most of them are relatively non-mobile with a few exceptions such as inorganic arsenic and chromium in its hexavalent form. The non-mobile metal(loid)s are a soil contamination problem rather than a water problem and have typically been dealt with by excavation and *ex situ* landfilling or treatments like electrophoresis, although *in situ* methods like phytoremediation have been tried on numerous sites (Marques et al., 2011). As opposed to organic contaminants the metal(loid)s cannot be degraded and their toxic effects have to be avoided by limiting the exposure. A total cleanup and removal of contaminants at metal(loid) contaminated sites will in many cases not be economically feasible, in particular if the sites have little value for construction and development, but also because

the contaminants are not easily removed from the soil (US EPA, 2002). Therefore, remedial actions which prevent the leaching of contaminants and reduce their presence in the porewater, are in some cases a feasible way to deal with such contamination. One of the lesser used methods to do this is by soil stabilization, where the contaminants are still present in the soil, but are trapped and unable to leach or only do so at non-detrimental fluxes.

Wood impregnating facilities, where the wood was treated with Chromated Copper Arsenate (CCA) to prevent fungi and insect damage of the wood, are examples of brownfields polluted with both mobile heavy metals (hexavalent chromium) and a metalloid (arsenic). In 2002 the estimated production of CCA-treated wood was around 20 million m^3 with a consumption of more than 300,000 tonnes of preservative chemicals (Humphrey, 2002). The use of arsenic for wood impregnation was completely suspended in Denmark in 1997. In 2003 production of CCA treated wood was banned within the European Union, while it was only banned for residential use in the United States. In Denmark one of the major wood impregnation companies was Collstrop, which operated 13 different sites in Denmark, the oldest, with tar-impregnation of railway sleepers, dating back to 1889. In recent years these Collstrop sites have gained considerable media attention in Denmark as most of the abandoned sites are heavily contaminated. The sites are contaminated by various organic and inorganic chemicals used in the production of impregnated wood (Danish EPA, 2010d). Most of the sites are left as abandoned brownfields with little or no remedial actions applied. The Hillerød and Brabrand sites have been the subject of much attention as questions were raised as to whether arsenic and other compounds present at the heavily contaminated sites could be leaching from the soil and transported by groundwater to nearby surface water bodies (Nielsen et al., 2010, Danish EPA 2010d).

There are several potential remediation technologies which could be applied at brownfields either by removing the contamination or controlling the leaching to reduce the risk associated with the chemicals. One technology is chemical stabilization that uses a reagent which binds the dissolved metal to the solid phase and in some cases also reduce hydraulic conductivity. Mixing the soil with cement is such a technique for improving the geotechnical properties, raising pH and reducing the leachable fraction of metals (Li et al., 2001, Malviya and Chaudhary, 2006). Another way is to add highly oxidized iron minerals with a

large surface area which increases the sorption capacity. Using iron minerals is therefore of interest, especially if a low cost product is available.

Such a low-cost form of iron oxides are iron water treatment residues (Fe-WTR), a waste product from the production of drinking water from groundwater, described in more detail in Chapter 4. Water treatment residues and other similar iron oxide by-products have previously been used in laboratory and lysimeter experiments for the amendment of arsenic contaminated soils with promising results (Doi et al., 2005; Kumpiene et al., 2006; Maurice et al., 2007; Sarkar et al., 2007a), but little attention has been given to pilot/full scale applications and the engineering aspects of applying the technology to a contaminated site. The fate of iron amendments under field conditions is also not well documented and recent studies suggest that the sorption capacity of iron amendments may deteriorate over time (Kumpiene et al., 2012).

The focus of this PhD project has therefore been to look into some of the more field related aspects of using Fe-WTR as a remedy to control leaching of CCA chemicals, a method which has never been applied at field scale anywhere in the world.

1.1 Objectives

This work investigates the use of water treatment residues (Fe-WTR) as a novel remediation method to limit the leaching of metal(loids) from CCA contaminated soils from pilot to full scale. This work seeks to widen the scientific base by documenting the effect on leaching of contaminants and investigating the fate of this amendment in CCA contaminated soil. The objectives of this thesis are therefore:

- To investigate if leaching of CCA contaminants from soil can be decreased significantly by amendment with Fe-WTR, at laboratory, pilot and full scale.

- To study the ageing of Fe-WTR in soil within the timeframe of a PhD study, as mineralogical changes in the Fe-WTR may influence leaching of contaminants.

This was accomplished by:

- Investigating the leaching of arsenic and chromium from a heavily CCA polluted and a less CCA polluted soil both amended with $5\%_{dw}$ Fe-WTR in a batch leaching experiment (Nielsen et al., I)

- Studying the effect of 2.5 $\%_{dw}$ Fe-WTR amendment on leaching of arsenic from a contaminated soil during 3 years of porewater sampling at a contaminated site and thereby investigating the effect of fluctuating conditions in a natural soil environment on *in situ* stabilization (Nielsen et al., I)

- Performing a field scale experiment challenging the practical application of amending contaminated soil with Fe-WTR *in situ* and measuring the effect on arsenic, chromium and copper leaching (Nielsen et al., II)

- Studying the changes from fresh Fe-WTR to Fe-WTR aged for 4 years *in situ* at a contaminated site by a kinetic reductive dissolution experiment, selective extraction and mineralogical characterization. (Nielsen et al., III)

2 Soil pollution by chromium, copper and arsenic

Chromium, copper and arsenic (CCA) are elements used in some formulations of wood impregnation chemicals and are therefore found together in contaminations originating from such e.g. (Lund and Fobian, 1991; Bhattacharya et al., 2002; Jang et al., 2002; Hopp et al., 2006). In this thesis the case of CCA polluted sites is used as an example for soil stabilization, but the technology is not site or industry specific and can be used for most types of metal(loid) contamination (Bone et al., 2004).

Field experiments of soil stabilization have been performed at the contaminated site of the former Collstrop wood impregnation facility in Hillerød, Denmark, a site that is extensively investigated compared to most other polluted sites. The site has gained public attention in relation to the implementation of the Water Framework Directive as an example of a polluted site that discharges contaminants (in this case arsenic) to surface water bodies. Detailed information on the site history, investigations and risk assessment of the site was published in 2010 (Nielsen et al., 2010).

In this section focus will be on soil pollution by CCA compounds from wood impregnation and the following subsections will provide an overview of the sources, soil chemistry and risk of CCA contamination.

2.1 Sources of CCA contamination

Chromated copper arsenates (CCA) have been widely used to preserve timber and wood products. In Denmark more than 100 sites have been registered as polluted by CCA (Amternes Videncenter for Jordforurening, 1997) and only a small fraction have actually been remediated. The size of the sites is highly variable, from small saw mills, covering some hundred square meters, to wood impregnation facilities with widespread storage facilities of several hectares. Contamination occurred from spill of impregnation liquid during handling or through leaking pipes and from the drippings of freshly impregnated wood (Amternes Videncenter for Jordforurening, 1997; Bhattacharya et al., 2002) and also wood debris and sludge from impregnation tanks deposited at the sites contribute significantly to the contamination mass (Hopp et al., 2008; Nielsen et al., 2010).

Impregnation liquid is a highly acidic (pH 1-2) solution of salts (CrO_3 and CuO) and arsenic acid (H_3AsO_4) that is forced into the wood by pressure. The exact formulation and methods has varied over the years and can be further explored in the review by Humphrey (2002). As the wood is impregnated to avoid destruction by fungi and insects, arsenic(V) is added as an insecticide and copper(II) as a fungicide. Chromium(VI) acts as the fixating agent as several complicated reactions, driven by the reduction of Cr(VI) to Cr(III) causes changes in the lignin structure of the wood (Humphrey, 2002).

Table 1: Properties of CCA components. References found in the text below and in Fig. 1.

	Redox State	**Dominant speciation and formulation**	**Behaviour in soil**	**Mobility in groundwater**
As	As(V)	H_2AsO_4 (pH<7) $HAsO_4^{2-}$ (pH>7) $CuHAsO_3$	Sorbs to iron oxides at pH >7	Moderate Moderate solubility
	As(III)	H_3AsO_3 (pH>9) $H_2AsO_3^-$ (pH <9)	Sorbs to iron oxides at pH 6-8	High
	As(-III)	$AsH_3(g)$	Gas phase	Not soluble
Cr	Cr (VI)	CrO_4^{-2} (pH>6.5)	Partly retained by iron oxides, reduced by organic matter	High, if no organic matter is present
	Cr(III)	$Cr(OH)_2^+$ (pH 4-6) $Cr(OH)_{3\ (s)}$ (pH 6-12)	 Forms solid phase	Low, low solubility
Cu	Cu(II)	Cu^{2+} (pH<7) $Cu_2(OH)_2CO_{3(s)}$ (pH>7) $CuHAsO_{3\ (s)}$	Sorbs to organic matter Can form solid phase in calcareous soil	Moderate, high for organic complexes Low solubility Moderate solubility

2.2 Fate of CCA in soil

The mobility and fate of CCA compounds are highly dependent on speciation of the elements and the soil properties like pH and redox-conditions and soil components like clay-types and organic matter content. Table 1 summarizes some of the chemical properties of the CCA contaminants and their behavior in soil and groundwater systems.

2.2.1 Arsenic

Arsenic, As, is a metalloid and will as such exhibit a different behavior than heavy metals. In the periodic table arsenic belongs to the same group (15) as phosphorous, and evidently there are some similarities in the behavior of arsenate, As(V), found in oxidized environments and phosphate in soil and groundwater. In reduced environments arsenic is found as arsenite, As(III). In water both the arsenate and the arsenite are protonated, see Fig. 1. The speciation is important to the mobility, as arsenite is generally much more mobile in soil and groundwater systems (Smedley and Kinniburgh, 2002). In the environment and in organisms, arsenite can be incorporated in organic arsenic compounds such as, monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA). The methylation process in the environment is in most cases microbially driven, but can also be performed by fungi (O'Neal, 1990). In most cases organic arsenic compounds constitutes less than 1% of the total soluble arsenic content in soil porewater (Turpeinen et al., 2002). Decomposition of organic matter facilitates the formation of arsenite in soil and therefore increase arsenic mobility (Balasoiu et al., 2001; Dobran and Zagury, 2006).

Arsenic is the most leachable of the CCA compound, as it has been found at several meters depth in soil profiles (Samfundsteknik, 1989b; Lund and Fobian, 1991) and in soil porewater (Andersen et al., 1996; Hopp et al., 2006; Clemente et al., 2008). Transported by groundwater, contaminants have been found downstream CCA sites in surface water (Nielsen et al., 2010) and sediment (Bhattacharya et al., 2002). At contaminated sites As is found associated with iron (hydro-)oxides (Bhattacharya et al., 2002) or aluminum-silicates like proto-imogolite allophane (Hopp et al., 2008), in the soil (Clemente et al., 2008; Kumpiene et al., 2012) and associated with impregnated wood debris (Hopp et al., 2008). XAFS-studies have further suggested that not only site-specific adsorption processes play a role in As retention. Arsenic bearing minerals like copper-arsenate precipitates and scorodite may sequester As(V) in the soil (Grafe et al., 2008) and mobility is then dependent on the solubility of said minerals.

2.2.2 Chromium

In the impregnation fluid chromium, Cr, is present as Cr(VI), which forms oxyanions like CrO_4^{2-} (pH >7) in water. Sorption of chromate is therefore, like arsenate, controlled by positively charged surfaces like iron and aluminum oxides, however organic matter content is often more important than sorption to

soil minerals for chromium mobility due to the reduction of chromate by organic matter. Chromate mobility is high in sandy soils with the leaching inversely proportional to the content of soil organic matter (Jang et al., 2002), due to chromate reduction as described above. Chromate can be reduced in soil by Fe^{2+}, sulphide (HS^-) or organic matter (Fendorf, 1995). This means that the occurrence of chromate is often connected to sandy soils, as the natural organic matter content of loamy soils will react with chromate to chromite, which forms insoluble Cr(III)-oxides at pH above 6. Manganese oxides have proven to be the only compounds capable of oxidizing Cr(III) to Cr(VI) in natural environments (Fendorf, 1995) and even pyrolysite, the most crystalline manganese oxide, has been shown to be an effective oxidant of Cr(III) (Saleh et al., 1989).

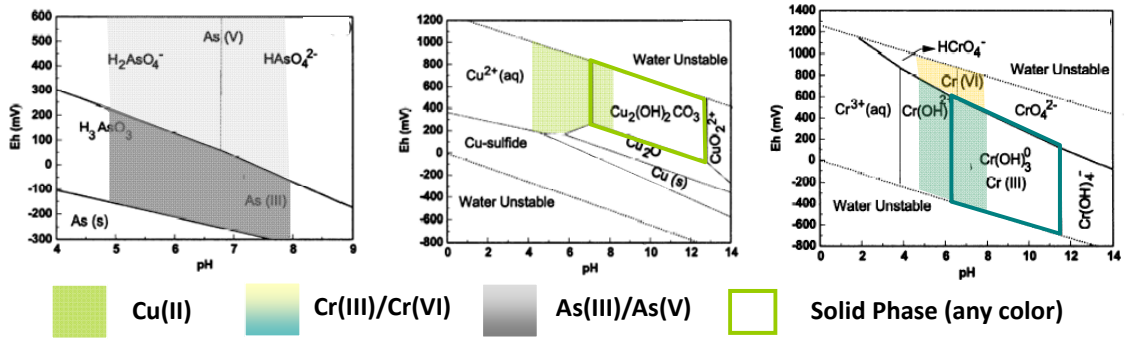

Fig. 1: pH-Eh diagrams of As, Cr and Cu in a water-air-CO_2 system at 25 °C and 1 bar. Colored species are most common at soil pH (pH 5-8). Modified from Bhattacharya et al. (2002) and printed with permission from Elsevier.

At CCA sites chromium is usually found to be rather immobile and therefore associated with the top soil and organic fractions (Lund and Fobian, 1991; Andersen et al., 1996) and wood debris (Hopp et al., 2008), presumably as Cr(III). Significant groundwater concentrations (approximately 300 µg/L) of unspeciated Cr below a CCA site have been reported (Hopp et al., 2006). The site had previously been treated with Fe(II) sulphate to decrease chromate mobility (Hopp et al., 2006), but the effect of the treatment has not been reported, thus the high concentrations may be a result of remaining Cr(VI).

2.2.3 Copper

In solution copper, Cu, is found as Cu^{2+} in oxic environments. Cu^{2+} forms strong complexes with surface active groups in organic matter (Baker and Senft, 1990), and copper mobility is therefore strongly correlated to dissolved organic matter (Clemente et al., 2008). In CCA contaminated soils, copper is often found in organic soil horizons (Lund and Fobian, 1991; Andersen et al., 1996) or in calcareous soils precipitated deeper in the soil profile as malachite $Cu_2(OH)_2CO_3$ (Lund and Fobian, 1991). A strong correlation of total organic carbon and Cu in porewater at a CCA site has also been reported (Andersen et al., 1996) indicating that copper may be mobilized by organic colloids or dissolved organic matter in shallow groundwater.

Table 2: Danish environmental criteria for CCA compounds in soil and water

	Speciation	**Soil general[1]**	**Soil direct contact[1]**	**Groundwater[1]**	**Drinking Water[2,3]**	**Surface Water[4,5]**
		[mg/kg]	[mg/kg]	[µg/L]	[µg/L]	[µg/L]
Arsenic	As_{total}	20	20	8	5	4.3
Chromium	Cr_{total}	1000	500	25	20	-
	Cr(VI)	-	20	1	-	3.4
	Cr(III)	-	-	-	-	4.9
Copper	Cu_{total}	1000	500	100	100	12

[1](Danish EPA, 2010c) [2] (Danish EPA, 2011b) [3]At connection to consumers property [4] (Danish EPA, 2010b)
[5]General (long term) quality criteria for freshwater

2.3 Risk of CCA contamination

As just described for elements such as arsenic, chromium and copper, pH and redox conditions determine the speciation of the elements which again affects the toxicity. For both arsenic and chromium toxicity is highly dependent on speciation. For chromium this is reflected in the water quality criteria presented in Table 2, which also shows that the quality criteria for arsenic and chromate in water are the strictest. Because As(V) is transformed to As(III) and further to various methylated species when ingested (Hughes, 2002) there is no meaning in separate values for arsenic species, despite large variation in toxicity, when considering the overall risk from arsenic pollution of soil and water. Because of their carcinogenic nature and high mobility in aquifers, arsenic and chromate are considered the contaminants of concern at CCA sites.

Fig. 2: Copper pollution and tree growth at the southern part of the Collstrop brownfield in Hillerød, Denmark. Based on observations of vegetation in 1989 (Samfundsteknik, 1989a) and the pollution investigation made later in the year (Samfundsteknik, 1989b).

In Bangladesh and East Bengal, where groundwater containing chronically toxic amounts of geogenic arsenic provides the source of drinking water, more than 37 million people are affected by arsenic (Smedley and Kinniburgh, 2002). Symptoms of chronic arsenic poisoning include skin, lung, bladder and skin cancer as well as skin diseases like hyperpigmentation and hyperkeratosis (US EPA, 2008). Arsenite is considered more toxic to humans than arsenate, and methylated arsenate species appear to be less toxic than the inorganic. More details on the rather complex human toxicology of arsenic can be found in the review by Hughes (2002).

Due to its highly oxidizing capacity Cr(VI) is carcinogenic and mutagenic in very low doses (US EPA, 2008). This is reflected in the low groundwater quality criteria of only 1 µg/L, as presented in Table 2. In the reduced form, Cr(III), Cr is much less toxic and an essential nutrient for living organisms (McGrath, 1990).

Copper is an essential micro-nutrient, but is toxic to living organisms at high doses. For plants the difference between essential and toxic dose is very small (Baker and Senft, 1990). An example of Cu toxicity to plants can be observed at the Collstrop brownfield in Fig. 2. The site displays a striking agreement between a lack of vegetation and high soil copper concentrations. An extensive study of the vegetation of the Collstrop brownfield, revealed that only *pohlia nutans*, a small moss, was tolerant to hot spot concentrations of contaminants (Jensen et al., 2010).

3 Soil Stabilization

Traditionally remediation of soil is considered to be the removal of contaminants from the soil matrix to make it comply with a soil quality criterion. In recent years this way of thinking has been challenged by cost/benefit analyses, and a new paradigm focusing more on contaminant flux than contaminant mass was introduced (Overheu et al., 2011). This opens up new perspectives in non-destructive soil remediation methods such as soil stabilization.

For heavy metal and metalloid contaminated soils remediation is complicated and expensive. Unlike organic contaminants, elements cannot be degraded, so the objective for remediation is usually to mobilize them from the soil matrix and then separate the element-containing phase. Fig. 3 presents an overview of the different treatment methods of heavy metal and metalloid contaminated soils. Most methods are aimed at specific elements, utilizing the geochemistry of the element to increase or lower mobility.

Stabilization of soil is done to trap contaminants in the soil matrix and thereby reduce leaching. The trapping can be done either physically by decreasing the hydraulic conductivity, chemically by adsorption or precipitation, or in a combination thereof known as stabilization/solidification or S/S. Soil stabilization is often combined with solidification to improve the geotechnical properties of the soil. Traditionally S/S is a method developed for hazardous waste products such as bottom ashes from waste incineration or heavy metal contaminated sludge, but it has been used at numerous, mostly heavily contaminated sites, including 45 arsenic contaminated US Superfund sites (US EPA, 2000).

In most cases S/S is done with Portland cement, alone or in combination with clays, ashes, silicates, lime and chemical reagents (Li et al., 2001; Malviya and Chaudhary, 2006) and a newer, not field validated, method includes a combination of polymers and resins (Shaw et al., 2008). For CCA contaminated soils, iron containing compounds have been proposed during the last decade, utilizing in particular the natural retention of arsenic by iron oxides.

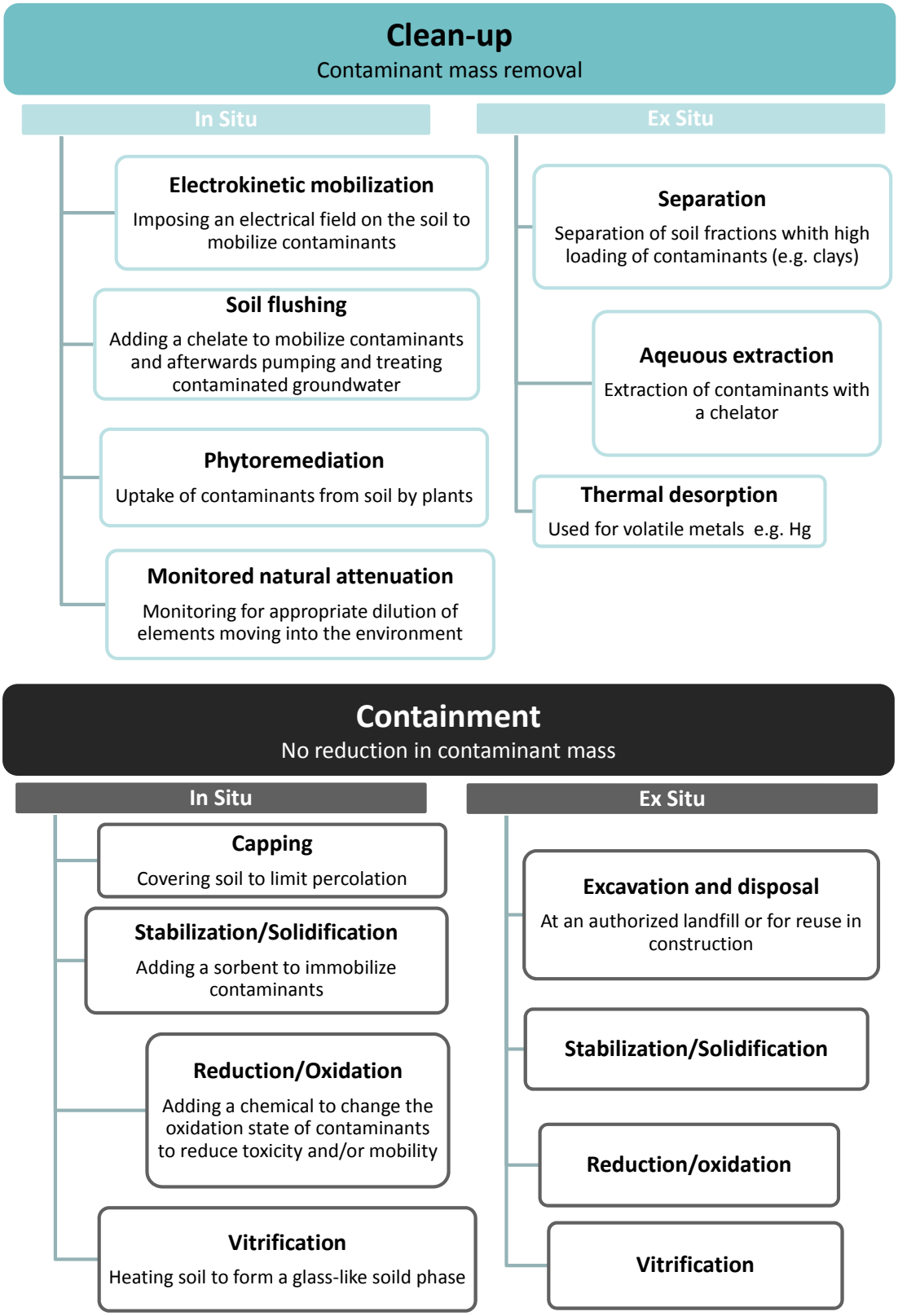

Fig. 3: Methods remediation of heavy metal and metalloid contaminated soil. Modified from (Lombi and Hamon, 2005) with methods from (US EPA, 2002) and (Marques et al., 2011).

3.1 Soil stabilization with iron amendments

Methods in which different forms of iron are added to the soil have been developed for chemical stabilization of soils and utilize the potential for contaminant immobilization by iron oxides. Miretzky and Cirelli (2010) as well as Komárek and co-workers (2013) compiled the options for As immobilization by numerous iron amendments and Kumpiene et al. (2008) listed the experiments with amendments for As, Cr, Cu, Zn and Pb contaminated soil. Iron amendments are generally preferred for As, Cr and Cu (Kumpiene et al., 2008) as described below.

The iron amendments work by increasing the amount of iron compounds in the soil. Either iron hydroxides adsorb the contaminants or/and in other cases co-precipitation of contaminant and iron containing phases occurs (e.g. scorodite, an iron arsenate). Adsorption chemistry and surface reactions of iron oxides are further explained in Section 4.4.

Iron grit (zero valent iron, ZVI) as well as liquid solutions of iron(II)/(III)sulphates form iron oxy-hydroxide phases after reactions with oxygen containing soil porewater (Leuping and Hug, 2005). ZVI oxidation has no major impact on soil pH (Kumpiene et al 2008), but iron sulphates and magnetite result in acidification of the soil which may lead to adverse effects e.g. mobilization of other contaminants like copper, cobalt, nickel and zink (Gemeinhardt et al., 2006; Lidelöw et al. 2007). Acid neutralizing substances, commonly lime, are therefore usually combined with iron sulphates (Warren et al., 2003; Hartley et al., 2004). However, if pH increases as a consequence of excess lime application, leaching of arsenic may not be decreased and even further increased (Gonzales et al., 2013). Acidification is avoided when applying ZVI or iron(III) oxides. Some of the iron oxides tested as soil amendment has been: Ochre from pyritic mine waters (Doi et al., 2005), iron blaster sands (Maurice et al., 2007; Lidelöw et al., 2007) or, as in this thesis, iron and/or aluminum water treatment residues (Sarkar et al., 2007a; Sarkar et al., 2007b) and iron water treatment residues (Nielsen et al., I and II).

3.2 Effects of iron oxide amendments

Contaminant immobilization by iron (hydr-)oxides may be measured in a number of ways: As direct measurements of the phase-distribution of contaminants in soil and water and or in plant uptake. The most widely used methods include: Reduction in plant uptake (Warren et al., 2003) and bioavailability using an *in vitro* gastrointestinal test (Sarkar et al., 2007b). Direct measurements of contaminants in leachate from lysimeters (Lidelöw et al., 2007) and porewater (Nielsen et al., I and II) or to determin the phase associated with contaminants by investigating the (immobilized) fraction of contaminants in iron (hydr-)oxide phases (Kumpiene et al., 2012).

In many cases the effect of the amendment is evaluated through bioavailability studies. Amendment with 1% ZVI was shown to decrease the bioavailability of As and Cr, but not Cu, in a CCA contaminated soil (Kumpiene et al., 2006). Amendment with 0.5% and 1% iron oxides applied as Fe(II)sulphates decreased the uptake of arsenic by 32% in field crops such as lettuce, calabrese, spinach and beetroot and the effect did not increase with increased iron amendment (Warren et al., 2003).

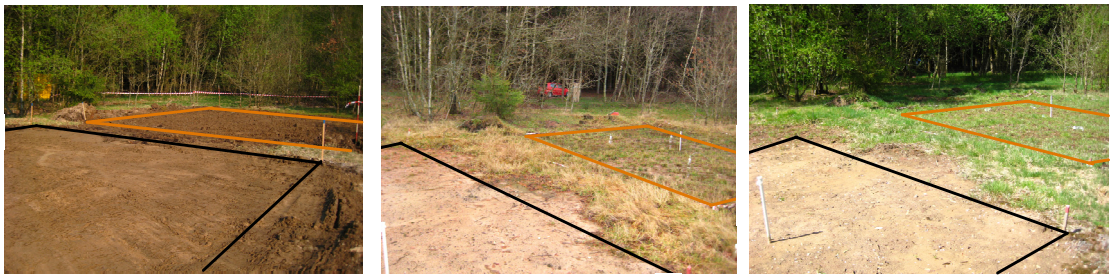

Fig. 4: Natural re-establishment of grass cover on unamended (black) and amended (orange) fields. Pictures are from May 2011 (left), November 2011 (middle) and May 2012 (right).

After soil mixing at the Collstrop site (Nielsen et al., II) natural regeneration of the grass cover happened mainly in the Fe-WTR amended plots. Fig. 4 shows the bare soil of the unamended plot in the foreground and natural regeneration of grass at the amended plot in the background in May 2011, just after soil mixing, unlike a year later in May 2012. The effect is likely to be a combination of decreased soil toxicity to plants, as the soil copper concentrations are decreased, but also improved growth conditions as a consequence of the plant nutrients (phosphate, Ca, Fe, and Mn) added with the Fe-WTR. Regeneration of plants is

generally considered an advantage of soil stabilization as it improves the esthetic value of the contaminated site and decreases the spreading of contaminants by erosion and dust formation (Renella et al., 2008). Increased evapotranspiration will also decrease the amount of percolating water thereby decreasing the leaching of contaminants. However, the plants do take up contaminants and increased biomass production will shunt these contaminants into the food chain by being consumed or via spreading of litter (Kumpiene et al., 2012).

Fig. 5: Field scale *in situ* amendment of CCA contaminated soil at the Collstrop site in Hillerød, Denmark. Data from this experiment is presented in Nielsen et al. (II). A, B and E shows the excavator mounted with the screening bucket used for soil mixing. C the rotary screening bucket. D is the Fe-WTR kept in suspension in the slurry mixing trailer. F shows the soil porewater sampling and G the Prenart® samplers before installation.

3.3 Field scale *in situ* stabilization

According to the scientific literature, only few of the iron based technologies for soil amendment have been tested at field scale. Field applications may not be reported and are as such difficult to include in literature reviews. Most field scale tests have been leaching tests performed in lysimeters (Mench et al., 2003; Lidelöw et al., 2007; Renella et al., 2008) and little attention has been given to the actual delivery strategy of the soil amendment for *in situ* application. A few exceptions does exist where iron grit, Fe(0), were applied to contaminated soils *in situ* (Warren et al., 2003; Kumpiene et al., 2012). Soil rich in iron oxides has also been used with moderate success as soil amendment of a river bed contaminated by overflow of pyritic mine waters (Aguilar et al., 2007). No information is available on how the amendment was applied in any of the *in situ* field experiments.

In the *in situ* field scale experiment at the Collstrop site, focus was on the soil mixing and the delivery of Fe-WTR to the soil. Mixing was performed with a rotary screening bucket made for separation of soil and larger fractions of waste or stones. To investigate if the mixing had any impact on the soil, two test fields was mechanically treated and Fe-WTR was added to only one of them. Pictures from soil mixing and collection of leachates are presented in Fig. 5. The screening bucket had the advantage that polluted concrete, originating from impregnation liquid holding tanks, and impregnated wood debris could be separated from the amended soil. Furthermore it was readily available for the contractor, implying significantly reduced operation costs.

Soil mixing at the site was not completely satisfying, as some of the lower parts of the treated field did not receive Fe-WTR (Nielsen et al. II). Soil iron content was measured in 9 homogenized cores from 0-50 cm below ground and from 50-100 cm below ground in each field. No significant difference could be found in the soil iron content between the cores from 50-100 cm below ground of the two fields. For improvement of the delivery strategy, the method can be used to greater depth or, though more costly, the soil amendment could be delivered using augers as used for ZVI granulate delivery to chlorinated solvent source zones (Fjordbøge et al., 2012) and traditional cement S/S (Bone et al., 2004).

It appeared that the mechanical treatment of soil increased the leaching of Cu, Cr and to some extent As, possibly by mobilization of contaminant bearing colloids,

fine particles of clays, iron oxides and organic matter that carry contaminants (Nielsen et al. II). Fe-WTR had an unexpected side effect on this, as this increased leaching was completely absent in the treated field. The effect is likely to be cementation by linkage of the Fe-Si atoms between ferrihydrite particles and the quartz-grains of the soil (Childs, 1992). A similar effect for reducing turbidity in freshwater caused by clay can be obtained by adding Fe-WTR to the suspension (Rhoton and Bigham, 2009).

3.4 Reductive transformation of iron amendments

When submerging an arsenic containing soil in water, arsenic concentrations in the supernatant water increases as a result of reductive dissolution of the iron oxides to which the arsenic is adsorbed (Hess and Blanchar, 1977). Long term release of arsenic in an anoxic soil has been observed with continuous release of arsenic in sediments (Brannon and Patrick, 1987) and the same mechanism has been observed for phosphorous in a wetland (Shenker et al., 2005). Adsorbed species associated with iron oxides undergoing total reductive dissolution are eventually released to the water phase and thereby mobilized for further transport in the aquifer, which make the use of iron amendments useless.

Ferrihydrite, the main component of Fe-WTR, may be completely dissolved by reductive dissolution upon reaction with organic matter in an anoxic environment (Willett, 1985). However, if reducing conditions are not strong enough to be sulphate reducing or methanogenic, or if the sorbed species are present, the iron amendment may persist despite reducing conditions. Ferrihydrite transforms to goethite at low concentrations of Fe^{2+} and magnetite at high Fe^{2+} concentrations (Benner et al., 2002), while Hansel et al. (2003) observed the formation of green rust at high Fe^{2+} concentrations. Pedersen et al. (2005) showed that the transformation to lepidocrosite and goethite was a catalytic effect of the Fe^{2+} in solution. Associated arsenic is not necessarily released (Coker et al., 2006) and may be incorporated into the magnetite structure during reductive transformation, but is excluded from the green rust structure (Kocar et al., 2010). During complete reductive dissolution of ferrihydrite, As was not released to solution until the ferrihydrite surface became too small to withhold the As load (Pedersen et al., 2006).

A major concern of using iron amendments is, that metal(loid)s will be released due to reductive dissolution when the soil becomes water saturated, either as an

effect of total dissolution or partial dissolution and recrystallization to iron minerals with less affinity for sorption. Release of As from soils amended with Fe(0) and oxygen scarfing granulate (magnetite) has been observed to increase greatly with increasing levels of soil moisture in a series of laboratory batch experiments and was explained by the reductive dissolution of iron oxides (Kumpiene et al., 2009). A similar effect would be expected for the field experiments conducted at the Collstrop site as the soil gets periodically flooded, but results are not so clear. Increased arsenic concentrations in soil leachate was found during the wet season for 3 consecutive years in the small scale field experiment (Nielsen et al., I), and for the full scale experiment dissolved iron in porewater did increase in the start of the wet season, but only in the unamended control plot, as can be seen in Fig. 6. (Nielsen et al., II). For the small scale experiment high levels of arsenic was released during the first winter, but during the following two winters seasonal release of arsenic were limited and As concentrations in the amended soil were still lower than in the unamended. This may be due to only partial reduction or formation of other iron oxides still able to retain contaminants, an explanation which is to some extent supported by the results from the ageing study (Nielsen et al., III).

Many soils are subject to repeated wetting and drying cycles that affect the soil mineralogy. Redox oscillations have been reported to result in transformation from nanocrystalline goethite to micro-crystalline goethite and hematite, rather than ferrihydrite in a Hawaian soil (Thompson et al., 2006) and have been observed for the iron rich horizon in a gleyic soil, where ferrihydrite was dissolved by prolonged flooding and reprecipitated mostly as goethite (Mansfeldt et al., 2012). A soil subjected to wetting and drying is therefore expected to lose retention capacity over the years due to the transformation from ferrihydrite to more crystalline iron oxides like goethite. These iron oxides still withhold contaminants, but to a lower degree and the resulting loss in potential sorption capacity is further discussed in Section 4.6.

Presence of adsorbed species like As may interfere with the iron oxide transformation and influence which secondary iron minerals are formed. If the ferrihydrite surface is loaded with As, the formation of green rusts instead of magnetite is more likely with a high As loading (Kocar et al., 2010). Arsenate sorbs well to the green rust surface (Jonsson and Sherman, 2008) at pH below 8 and in small amounts it will even hinder oxidation of Fe(II) in the green rust

structure (Su and Wilkin, 2005). Therefore, the iron amendment may be transformed but the newly formed phase will still sorb the contaminants. Repeated wetting and drying cycles may also act to trap contaminants in soil, as it has been reported for Cu in contaminated soil amended with iron-rich waste water residues (Contin et al., 2007) where DTPA-extractable Cu decreased with 95% in a grassland soil after one to three redox cycles.

Transformation of ferrihydrite may happen within days when catalyzed by Fe^{2+} (Pedersen et al. 2005) and result in total dissolution and/or formation of other iron oxides, resulting in partial or complete mobilization of associated contaminants as discussed above. Another important effect on the fate of contaminants stabilized by Fe-WTR may be the recrystallization of ferrihydrite at fully aerobic conditions. This transformation is much slower with a rate of several years or even decades, depending on temperature, pH and presence foreign ions (Schwertmann et al. 2004, Schwertmann et al. 2000). The discussion of ferrihydrite transformation to other iron phases under aerobic conditions is further elaborated in Section 4.5.

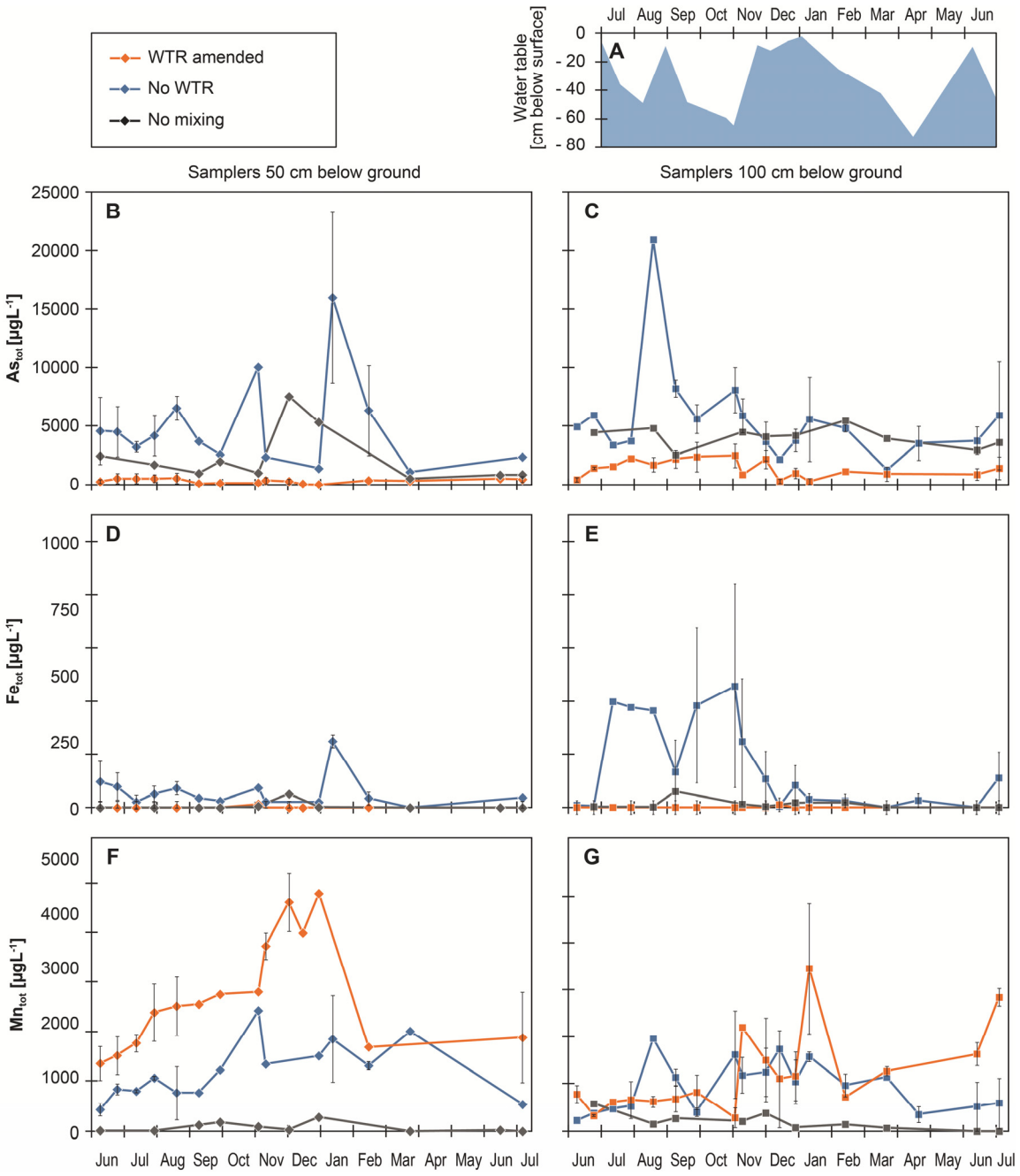

Fig. 6: Arsenic, iron and manganese soil porewater concentrations and the secondary water table in the amended, mixed and undisturbed soil (Nielsen et al. II). Left column (BDF) presents data from samplers 50 cm below surface and the right column (CEG) 100 cm below surface. The water table (A) is an average of 4 shallow wells situated in both fields.

4 Iron water treatment residues

The Danish drinking water supply is entirely based on groundwater. Groundwater in equilibrium with aquifer materials contains dissolved species depending on the mineral composition of the aquifer and to make the groundwater into drinking water some of the natural components are removed. Before water reaches the consumer, it has been aerated to precipitate dissolved species like iron, manganese and calcium and strip off dissolved gasses like CO_2, hydrogen sulphide and methane. The precipitates are filtered from the water and form the by-product known as water treatment residues, commonly abbreviated WTR or Fe-WTR to indicate the major component. In terms of composition, mineralogy and morphology, iron water treatment residues are analogue to naturally occurring ochre formed in springs (Childs et al., 1982; Carlson and Schwertmann, 1987), where anoxic groundwater comes into contact with oxygen from the atmosphere.

4.1 Production and disposal

Aeration of water is traditionally done by cascading the water to reach oxygen saturation. Once the water is saturated, oxidation of iron, which is usually the main dissolved component, happens as a biotic and/or abiotic process. Biotic oxidation of Fe^{2+} is facilitated by iron oxidizing bacteria such as *Gallionella*, *Leptotrix* and *Siderocap spp*. and is generally preferred in water treatment plants, as it leads to a higher precipitation rate, which makes retention time in the filters shorter (Sogaard et al., 2000).

After aeration the water is passed through sand filters, where precipitates like ferrihydrite, calcite and manganese oxides are removed from the water. Every few weeks, as needed, the filters are back-flushed and the solids left to settle in a sedimentation basin (Danva, 2011). In small waterworks the residues are commonly just stored on the premises, either waterlogged in basins or dried. It is also possible to obtain permission to discharge WTR containing flushing water into the sewage system (Danva, 2011). No records exists on the amount of water treatment residues produced in Denmark, but an estimate based on the average iron content in groundwater suggests around 500 tonnes dry matter per year (Aktor, 2007).

Trace elements are a major concern for the reuse of water treatment residues. In Denmark geogenic trace elements like Al, As, Pb, Cd, Cu, Ni and Zn are reported to be found in levels exceeding the drinking water criteria in wells used for drinking water supply (Thorling et al., 2011) and may also be found co-precipitated in significant amounts in the WTR (Aktor, 1990). In some waterworks the formation of iron oxides is actively used in removal of geogenic arsenic, which can result in arsenic concentrations in the WTR of 0.1-1% (Aktor, 2007). With a content of carcinogens of more than 0.1% some WTRs classify as hazardous waste, which must be landfilled at controlled sites (Danish EPA, 2011a) and the use as a soil amendment is not likely to be feasible. In areas, where the background levels of toxic trace elements are high, it is highly recommended to perform a screening for trace elements before the WTR is considered for soil amendment. Data on the occurrence of geogenic trace elements in Danish groundwaters can be obtained from the Danish Geological Survey e.g. Thorling et al. (2011).

4.2 Composition of Fe-WTR

Iron water treatment residues are a brownish-red sludge-like suspension with highly variable water content. In settling basins at the water works, the suspension is kept with water content large enough to be able to pump it between basins (usually 80-90% water) and to the final storage basin, where it is left to dry out.

Depending on water chemistry, the principal part of the solids is usually iron oxides, but manganese oxides (Aktor, 1990) or aluminum oxides (Nagar et al., 2010) can occur in similar amounts as iron oxides. Hydrated silica and calcite are also commonly found co-precipitated with the metal oxides. As the formation of water treatment residues in many cases is a biotic process, organic matter from the microbial community may also be present. A selection of element compositions of some iron water treatment residues is presented in Table 3. The table shows that the variation in the iron content is low compared to the variations in trace elements.

Table 3: Composition of iron water treatment residues.

	Fe	Al	Mn	Si	P	As	Cu	Cr	Ni	Pb	Cd
	%					mg/kg					
Sjælsø, DK[1]	32.2	-	1.1	4.06	-	21.8	-	5.2	-	-	-
Sjælsø, DK[2]	28.6	-	0.85	-	-	46.1	36.6	b.d.	-	-	
Solbjerg, DK[1]	32.1	-	1.41	5.1	-	580	-	4.1			
Average for 39 Danish waterworks[3]	37.4	-	0.75	-	3.3	282	39	16	41	7	4
Average for 5 Fe-WTRs[4]	22.1	6.1	1.09	-	0.07	-	46	38	64	47	-

[1] (Nielsen et al., I) [2](Nielsen et al., II) [3](Aktor, 1990) [4] (Ippolito et al., 2011) b.d. below detection limit – not measured

4.3 Structure and mineralogy

A high rate of Fe(II) oxidation and the presence of Si favors the formation of ferrihydrite (Cornell and Schwertmann, 2003) and the water treatment residues have repeatedly been confirmed by XRD to consist of 2-line ferrihydrite (e.g. Nielsen et al., I; Carlson and Schwertmann, 1987), an iron oxyhydroxide characterized by a poor crystallinity reflected in the name which refers to the number of lines appearing in an XRD analysis. In waterlogged settling ponds at the water works, the iron water treatment residues may consist of green rust, a partly reduced Fe^{2+}/Fe^{3+} containing iron oxide. In contact with air green rust transforms to a mixture of goethite and ferrihydrite (Koch and Morup, 1991). Ferrihydrite is meta-stable and transforms rather easily to other iron oxides as further discussed in Section 4.5. The crystal size of the ferrihydrite particles is very small, 4-6 nm (Cornell and Schwertmann, 2003), but the nano-sized crystals are aggregated in 100-200 μm particles (Sogaard et al., 2000). Aggregation forms micropores, which creates internal surfaces in the Fe-WTR. This allows for diffusion driven sorption, as observed for phosphate (Makris et al., 2004). Because of the very small crystal size and aggregated structure, the specific surface area is very high compared to other iron oxides. Natural ferrihydrites are reported to have a BET surface area between 68 and 425 m^2/g (Carlson and Schwertmann, 1981) and Fe-WTR used for experimental work in this thesis ranged from 153 to 231 m^2/g (Nielsen et al. I and II). The surface area is a key parameter in evaluating the sorption potential because it indirectly measures the number of available surface sites.

4.4 Surface reactions of Fe water treatment residues

An iron oxide surface in contact with water is covered by a layer of water molecules that partly reacts with hydroxyl groups at the surface. Depending on the pH of the solution, this water layer protonates or deprotonates, and the surface charge of the iron oxide is thereby dependent of pH. The iron oxide surface has a net positive charge below the pH value termed at the point of zero charge (PZC) and a net negative charge above. The PZC for natural ferrihydrites, coprecipitated with silica, lies between 5.3 and 6.3, while the PCZ of synthetic ferrihydrites without associated silica was found to be higher, between 7 and 8 (Schwertmann and Fechter, 1982). Therefore ferrihydrite has an overall positive surface charge in soil and ground water environments, which makes it, as well as other iron oxides, a good sorbents for anions.

The hydroxyl-groups at the iron oxide surface allows for specific sorption, where an ion is adsorbed to the surface by ligand exchange. Arsenate and arsenite as well as chromate sorbs strongly to iron oxides, but the sorption density is dependent on pH (Dixit and Hering, 2003). Arsenate and chromate are adsorbed at low pH and arsenite has a sorption maximum at circumneutral pH. Both arsenate and chromate form an inner sphere surface complex at the ferrihydrite surface. Arsenate and arsenite form bidentate complexes (Waychunas et al., 1993) on ferrihydrite and, as expected, also on Fe-WTR (Makris et al., 2007). An overview of the surface complexes formed by As on the ferrihydrite surface is presented in Fig. 7.

For chromate, inner-sphere complexes of both bidentate and monodentate configuration has been observed on ferrihydrite (Hsia et al., 1993; Fendorf, 1995). Cr(III) and Cu(II) are divalent ions and form positively charged complexes in water, that may sorb to negatively charged sites of the ferrihydrite surface. Cr(III) sorption to ferrihydrite reaches maximum at pH >5 and Cu(II) at pH >6 (Aoki and Munemori, 1982).

The adsorption of ions may lead to pH increase, as observed for As (Jain et al., 1999). The mechanism behind the change in pH is the OH^- ion being released during the specific adsorption. Slight pH increases were seen in the batch leaching experiment (Nielsen, et al. I), but the effect is likely to be buffered in natural systems.

Other ions may be competing with CCA compounds for sorption sites on iron oxides. Phosphate (Sarkar et al., 2007b), organic matter (Mohapatra et al., 2007) bicarbonate (Appelo et al., 2002) and silicic acid (Jones et al., 2009) are some of the ions commonly considered.

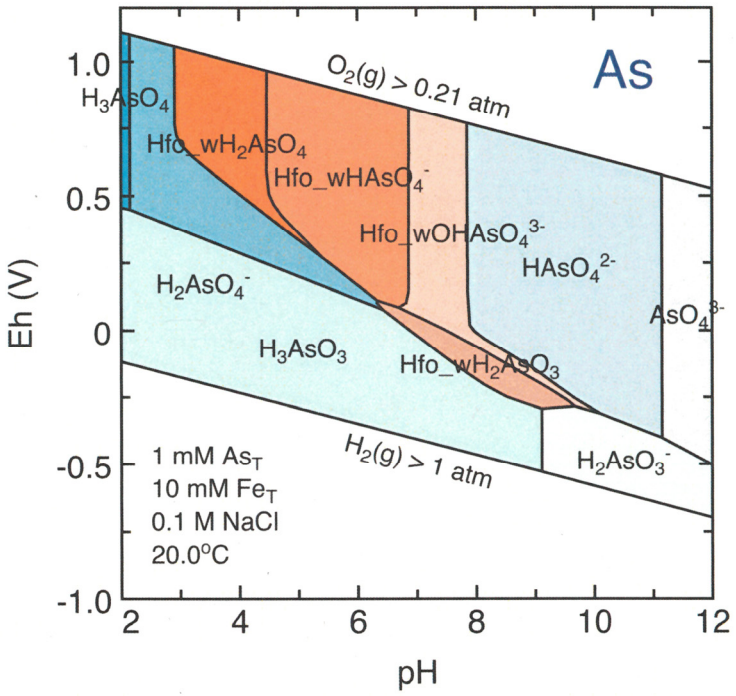

Fig. 7: Dominant speciation of As on the ferrihydrite surface. Orange colors indicate ferrihydrite-As surface complexes and blue colors the field where ferrihydrite is not formed (Smedley, 2006). With permission from the International Association of Hydrogeologists, The Netherlands.

4.5 Ageing of ferrihydrite

Ferrihydrite is a metastable iron oxyhydroxide solely found in Holocene sediments. Eventually it will be transformed to other iron (hydr-)oxides, most commonly goethite and hematite, with a temperate climate favoring the formation of goethite over hematite (Cornell and Schwertmann, 2003). The transformation of pure ferrihydrite at a wide range of pH and temperatures was studied by Schwertmann et al. (2004) in a long term *in vitro* experiment. Part of the results are presented in Fig. 8 stating the half-life of pure ferrihydrite is approximately 2600 days, more than 7 years, at pH 6 and 4 ^{o}C, while at 10^{o}C and identical pH transformation was faster with a half-life of only 1300 days, about 3.6 years (not shown in Fig. 8). As the yearly average temperature is typically just below 9 ^{o}C in Danish soil and groundwater systems, ferrihydrite ageing in a Danish soil would be expected to be in line with these findings. The oxalate extractable fraction of Fe in Fe-WTR, corresponding to the ferrihydrite content, decreased from 95% in fresh Fe-WTR to between 40 and 50% within 4 years of ageing under field conditions (Nielsen et al. III). At 50 cm depth, where the Fe-WTR was aged, daily temperature variation is somewhat leveled out, but seasonal variation may be more than 13 ^{o}C (Kristensen, 1959). The effect of temperature is therefore difficult to compare directly to the results from *in vitro* experiments performed at constant temperature, but the measured half-life of oxalate-extractable Fe of about 4 years is still within the results observed by Schwertmann et al. (2004) at pH 6 at 4^{o}C and 10 ^{o}C. The influence of pH may also be substantial, but at slightly acidic pH as found at the Collstrop field site (Nielsen et al., I), temperature has a larger impact (Schwertmann et al., 2004).

In natural environments the transformation rate depends on other factors apart from pH and temperature. Redox conditions (as discussed in Section 3.6) and loading of adsorbed species may impact not only transformation time but also end-product of the transformation. Another long term study (16 years) showed that ferrihydrite recrystallization rate decreased significantly in presence of clay minerals, especially allophane and smectite, and the effect was attributed to soluble Al and Si originating from the clay minerals (Schwertmann et al., 2000). Foreign ions block the sites for crystal growth and thereby slow the recrystallization process. Arsenate (Ford, 2002), silica (Vempati and Loeppert, 1989) and organic matter (Jones et al., 2009) as well as Cu(II) (Cornell and Giovanoli, 1988), all typically present in CCA contaminated soil, may act as inhibitors for ferrihydrite transformation. Therefore the transformation rate of

ferrihydrite is expected to be slower in a soil environment with an abundance of adsorbed species. This has been observed for a 10 year old ochre precipitate originating from mining activities in which no transformation of ferrihydrite was observed, and explained by loading of As associated with ferrihydrite (Moldovan et al., 2003). Adsorbed ions were plentiful in the aged Fe-WTRs, as Fe-WTRs scavenged As, Cr and Cu ions, but not quite to the extent of the aforementioned mine drainage precipitate, as discussed in the next section. The amount of adsorbed ions did not seem to decrease the transformation rate markedly compared to the *in vitro* experiments. Combined with the effect of periodically reduced conditions that may have increased transformation rate of Fe-WTR (Nielsen et al. III), the total effect levels out to approximately the same half-life as found by Schwertmann et al. (2004).

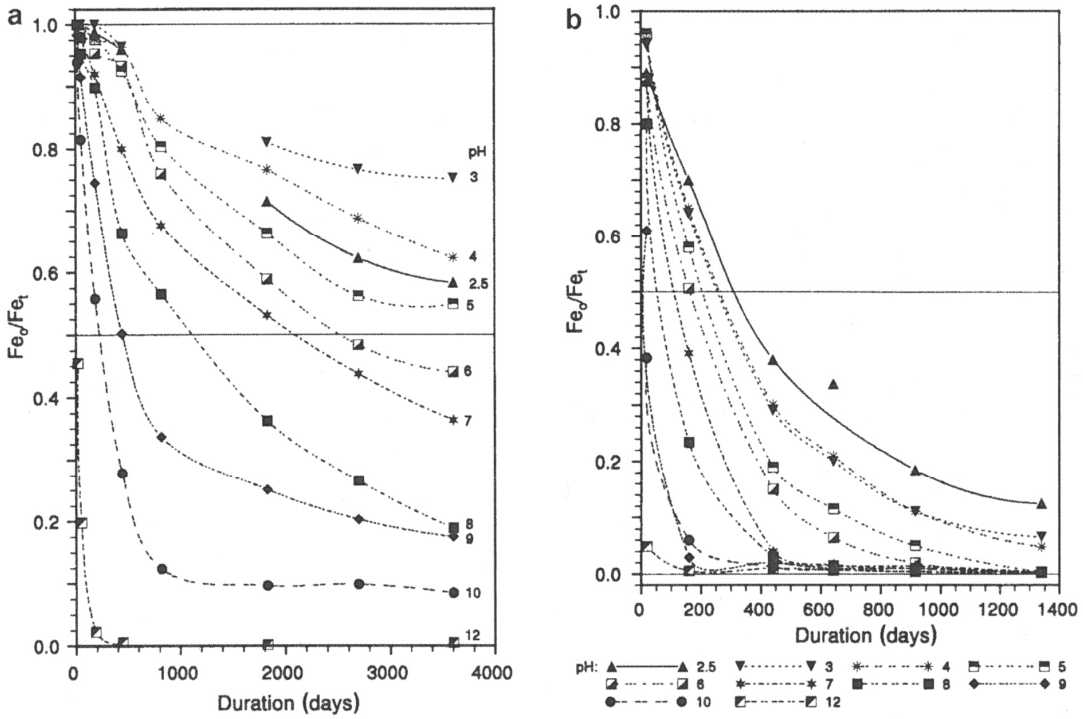

Fig. 8: *In vitro* transformation of ferrihydrite (Fe_O) to crystalline phases (Fe_t) at 4°C (a) and 25 °C (b). Please note the different timescales. Reproduced with the kind permission of the Mineralogical Society of Great Britain & Ireland from a paper in Clay Minerals by Schwertmann et al**.** (2004).

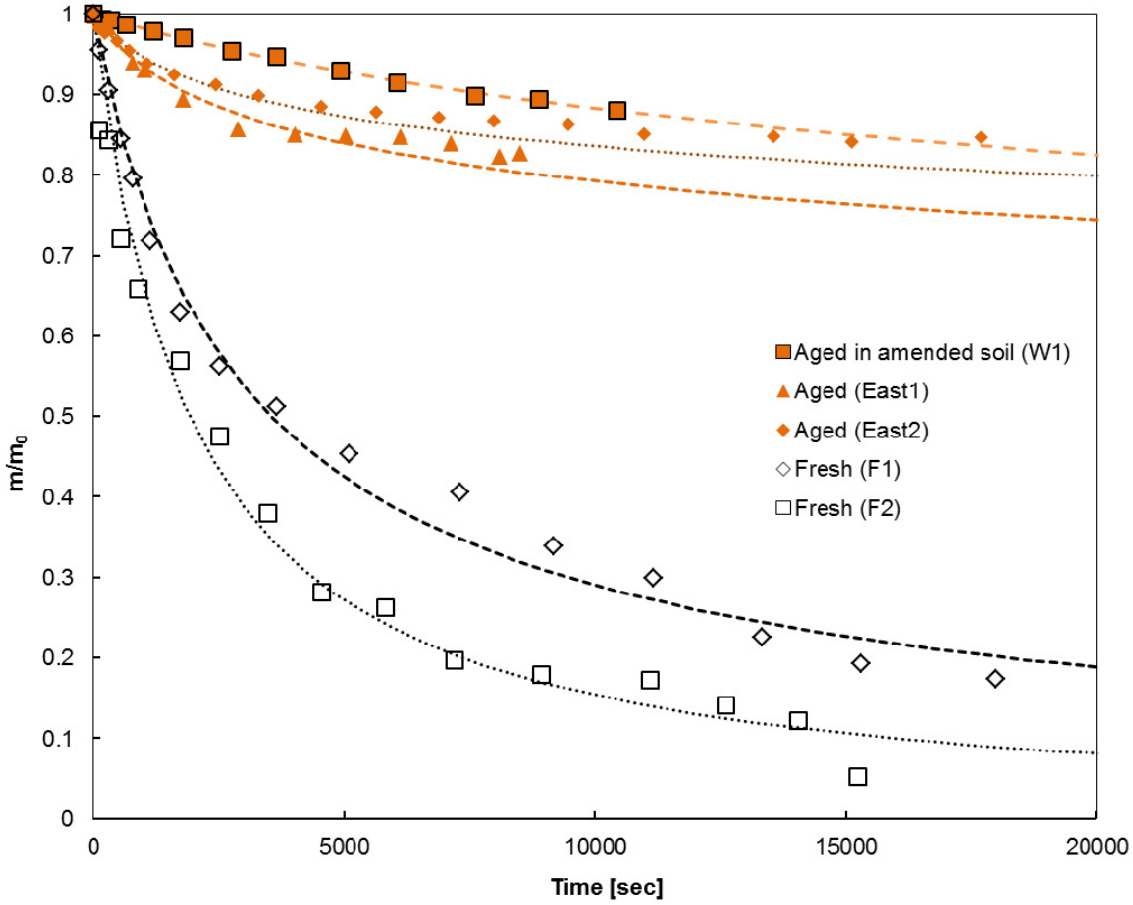

Fig. 9: Remaining mass (m/m_0) of fresh and aged Fe-WTRs as a function of time during reductive dissolution in 10 mM ascorbate at pH 3 (Nielsen et al., III). Lines are best fit of the rate law derived by Larsen and Postma (2001).

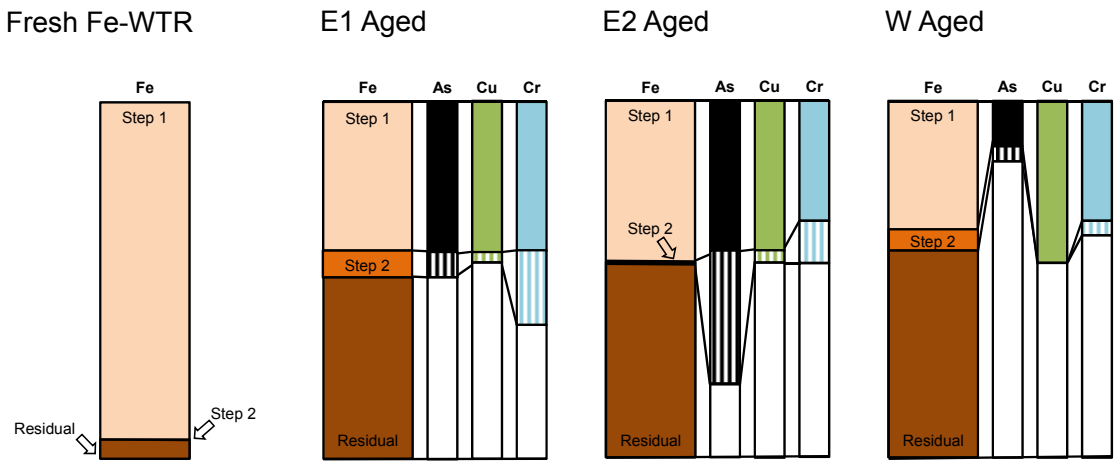

Fig. 10: Selective extraction of aged and fresh Fe-WTRs. Wide bars indicate Fe and narrower bars the associated contaminants (As, Cr and Cu) divided in extraction steps. Step 1 is the oxalate extractable fraction, while step 2 is extracted with oxalate and ascorbate. For the fresh Fe-WTR the content of As, Cr and Cu was negligible (Nielsen et al. III).

4.6 Effect of ageing on contaminant association

If, as the literature and ageing experiment (Nielsen et al. III) suggest, ferrihydrite is transformed to goethite with time, sorption capacity is expected to decrease, which may result in desorption of As during the transformation process (Fuller et al., 1993). As described in Section 4.4, most of the species of CCA compounds may sorb specifically to the surface of ferrihydrite, but the amount of adsorbed species is dependent on the number of available sorption sites. Based on a compilation of sorption experiments Dzombak og Morel (1990) estimates the site density for ferrihydrite to be 0.2 mol sites/mol Fe with a surface area of 600 m^2/g. Experimental values for equilibrium arsenic loading on ferrihydrite was found to be 0.24 molAs(V)/molFe and 0.31 molAs(III)/molFe (Dixit and Hering, 2003). Naturally occurring ferrihydrites are reported to adsorb very large amounts of arsenic e.g. mine tailings with a loading of 5.3-303 molAs/molFe (Moldovan et al., 2003). For very high arsenic loadings surface precipitation of arsenates may form (Raven et al., 1998) which lead to erroneously high As loadings, and that may also be the case for the high arsenic loads fournd in mine tailings. Maximum sorption capacity for arsenic on goethite has been reported by Dixit and Hering (2003) to be 0.016 molAs(V)/molFe, about 15 times lower than for ferrihydrite. Transformation of goethite from ferrihydrite happens by dissolution of the ferrihydrite structure and reprecipitation starting from a goethite nucleus (Schwertmann et al., 2004). This implies that when ferrihydrite gradually dissolves, adsorbed species will to some extent be relocated to the newly formed goethite surface, but others will be released to the water phase, unless the goethite surface is large enough to withhold the amount of contaminants. As more or less the same surface reactions apply to goethite, the amended soil will still retain some sorption capacity.

Transformation of the least crystalline iron fraction is proposed to lead to increased contaminant leaching, as suggested by observations from soil amended with a mix of ZVI, coal fly ash and compost during 10 years of monitoring (Kumpiene et al., 2012). Combined μXRF probing and selective dissolution revealed that As in the ZVI amended soil was to a higher extent associated to ferrihydrite than goethite, and the authors proposed the transformation of ferrihydrite to more crystalline iron oxides to be the cause of increased As leaching (Kumpiene et al, 2012). Selective extraction of Fe-WTRs aged for 4 years does not show a stronger association of As, Cr and Cu with the least crystalline (oxalate-extractable) fraction of iron (Fig. 10), as the contaminants are

more or less evenly distributed between the oxalate extractable iron fraction and the remaining, more crystalline iron fraction. This indicates, that that sorption capacity of the aged Fe-WTR is not dramatically reduced with time, at least not after 4 years of ageing.

Some ageing effect was indicated by the batch leaching experiment, where arsenic concentrations in the supernatant increased for two soils amended with 5% Fe-WTR (Nielsen et al, I). This experiment was conducted at room temperature, at which the ageing, as discussed in the previous section, is accelerated. Effects of ageing on contaminant leaching in field experiments (Nielsen et al. I and II) are difficult to identify because of natural variation and fluctuations in water percolation and redox conditions. In the much more controlled environment of the batch experiment the slight increase in arsenic leaching with time (Fig. 11) more easily identified.

To increase the effective lifetime of a Fe-WTR amendment, an excess amount of Fe-WTR should be applied to the soil to counteract the recrystallization effect, but a more precise estimate of this excess amount remains an area available for future investigations.

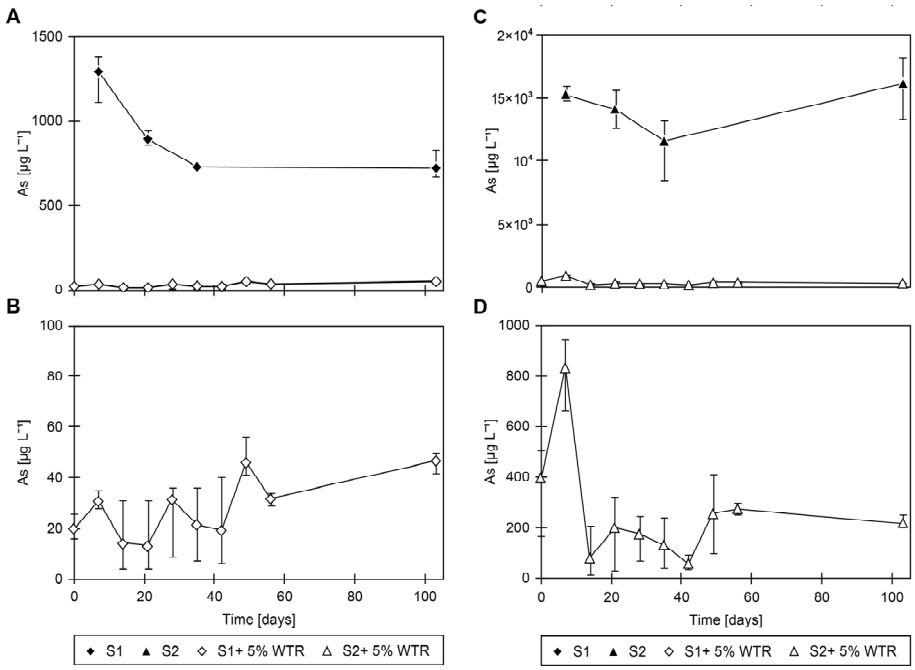

Fig. 11: Supernatant concentrations (L/S= 4.5) of treated and untreated soils during 103 days of ageing in a batch experiment on soils S1 (255±14 mgAs/kg) and S2 (1033±69 mgAs/kg) (Nielsen et al., I). With permission form Elsevier.

5 Feasibility of soil stabilization with Fe-WTR

The following sections present an overview of the current practice for handling and remediation of heavy metal polluted soils, as well as a discussion of the possible future use of soil stabilization with Fe-WTR.

The British Environment Agency has published a report by Bone et al. (2004) with guidelines and recommendations in order to promote the Stabilization-/Solidification (S/S) method, as it is infrequently used despite its obvious benefits of being of low technical execution and low cost. The report sums up this list of reasons why soil stabilization is not more frequently used:

- Low cost and widespread use of disposal to landfills.
- Lack of authoritative technical guidance.
- Uncertainty over the durability and rate of contaminant release from S/S treated soils.
- UK experience of past poor practice in the application of cement stabilization.
- Residual liability associated with the immobilized contaminants remaining on-site, rather than their removal or destruction.

All of these, except perhaps the cement stabilization practice, apply to Danish conditions, where stabilization of soil is also rarely used. No detailed technical guidance exists in Danish, except for a short literature review based on American experiences (Danish EPA, 1998). The durability and rate of release are certainly one of the great unknowns, but research is ongoing and good estimates may be available in the near future and has certainly developed since 1998. The last reason is a key issue, as pointed out by Rivett and co-authors (2002): “perception of residual risks from contaminants left on site which impact on property value and potential future liabilities are also underlying reasons for the preference for off-site disposal”. Another argument is presented by Onwubuya and co-authors (2009), who suggests that the wide spread use of so called “gentle” remediation

and soil treatment options (including soil stabilization) are not considered, as they are not included in decision support tools used by decision makers. This might be part of the explanation, but other factors like economy and applicability also impacts decision making.

5.1 Current practice for metal(loid) polluted soil

An English study, interviewing decision-makers on the use of remedial strategies, confirmed the anecdotal accounts of landfilling being the most common "remediation" strategy. More than 80% of all contaminated sites were excavated and landfilled (Rivett et al., 2002). Of 100 sites contaminated with metals, only 2 sites were stabilized/solidified. The type of amendment is not stated, but is most likely cement. Decisions on the choice of remediation techniques may be governed by other factors than purely technology-based decision making e.g. tax on landfilling or legal practice, but the overall trend in contaminated soil management is, that it is mainly based on landfilling. During the year of 2006 17% of excavated soil in Denmark was landfilled directly as the concentration of contaminants was too high for re-use of the soil e.g. for construction works (Danish EPA, 2008). Further information on the type of contamination that was landfilled was not stated.

Table 4: Classification of polluted soils for excavation and landfilling. Data presented are for CCA compounds only.

	Polluted soil				**Hazardous waste[2]**
	Class 1[1] Unpolluted	**Class 2[1]** Slightly poll.	**Class 3[1]** Polluted	**Class 4[1]** Polluted	
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
Arsenic	20	20	50	>50	>1000
Cr(VI)	20	35	50	> 50	>1000
Cr_{total}	500	500	750	>750	n.d.
Copper	500	500	750	>750	n.d.

[1] (Københavns Amt et al., 2001) [2] (Danish EPA, 2011a) [n.d.]Not defined

Polluted or pre-classified (of urban origin and therefore likely to be contaminated) soils are not to be excavated without noticing the authorities, who will assign the soil to a receiving facility. The polluted soil is classified according to the maximum contaminant content. In multi element contamination, the element that classifies for the highest class determines the overall class. The maximum criteria for CCA compounds for the different classes are presented in

Table 4. Heavy metal polluted soil in class 3 is categorized as ”polluted soil for cleaning and/or landfilling”, but the guidelines also state that heavy metal contaminated soils of class 3 and above are not to be cleaned, as the remediation methods are “yet too expensive compared to the environmental benefits” (Københavns Amt et al., 2001).

5.2 Re-use of stabilized soil

If polluted soil is to be reused in construction it has to comply with the specifications for reuse (Danish EPA, 2010a) and is designated to a *category*, as they appear in Table 5. The reuse categories are first of all defined by the metal content of the soil and secondly by the leaching of contaminants as determined from a 24h batch leaching test as described by Danish standards (Dansk Standard, 2002). For re-use of an arsenic polluted soil with a total arsenic concentration above 50 mg/kg, the leachate concentration must not exceed 50 µg/L. In the initial batch experiments, the stabilized, lightly polluted soil with 255 mg/kg As and 27 mg/kg Cr did not produce a leachate with higher concentrations than 50 µg/L during 100 days (Nielsen et al. I). This indicates that amendment of a *Class 3* soil with 5% Fe-WTR under normal pH and aerobic conditions e.g. in a baffle wall or below roads, will make it comply with the leachate criteria to be classified as a *Category 3* soil, as the leachate will not exceed the criteria.

Table 5: Criteria of soil for re-use in construction (Danish EPA, 2010a). Leachate concentrations are estimated by DS/EN 12457-1 (Dansk Standard, 2002).

Soil concentration	**Category 1**	**Category 2**	**Category 3**
	[mg/kg]	[mg/kg]	[mg/kg]
Arsenic	0-20	>20	>20
Cr(VI)	0-20	>20	>20
Cr_{total}	0-500	>500	>500
Copper	0-500	>500	>500
Leachate from reused soil	**Category 1**	**Category 2**	**Category 3**
	[µg/L]	[µg/L]	[µg/L]
Arsenic	0-8	0-8	0-50
Cr(VI)	n.d.	n.d.	n.d.
Cr_{total}	0-10	0-10	10-500
Copper	0-45	0-45	45-2000

[n.d.] Not defined

Polluted soil with a content of carcinogenic substances like arsenic or chromate exceeding 1000 mg/kg is considered hazardous waste and has to be handled with special precautions (Danish EPA, 2011a). Hot spot soils from the Collstrop site in Hillerød contain more than 2000 mg/kg As (Samfundsteknik, 1989b) and will be considered as such. Soil classified as hazardous waste is not allowed for reuse (Danish EPA, 2010a). Amendment of this type of soil may be useful as an *ex situ* technology at soil treatment facilities, where soil is landfilled under a full monitoring scheme.

5.3 *In situ* stabilization

Use of soil stabilization as an *in situ* method is presented in Nielsen et al. (II) and despite the limited amount of amendment a rather large decrease in porewater element content was obtained. Because of high water content, a less than optimal amount of solids was administered and hence the Fe-WTR dose was only 0.6 wt%, much less than the 5 wt% in the initial batch tests and the 2.5 wt% small field experiment (Nielsen et al., I). The necessary amount of Fe-WTR to reach the ground water quality criteria in the leachate depends on the contamination level, soil pH, and the amount of competing ions and systematic testing of those factors are needed to be able to calculate the proportion of Fe-WTR needed for a satisfactory stabilization of contaminants. Also the aforementioned ageing of ferrihydrite and possible contaminant release has to be taken into account.

As the polluted amended soil does not meet the soil criteria for direct contact (as presented in Table 2) special precautions have to be made considering the land-use. The method is not for use in cases where a site is being developed for construction as the soil will still be toxic. Hence the stabilized site will have to remain closed for public access or screened off by a protective layer for instance a clean soil cover or pavement.

In situ stabilization with iron amendments is not a method that will completely stop the leaching of contaminants, but instead it can lower the leaching to a level, where it no longer poses a threat to the surrounding environment. The method will require ongoing monitoring, but large contaminated sites that are mapped in the national list of polluted sites, are already the subject of a ground water monitoring scheme, which minimize installation costs of monitoring.

5.4 Economic aspects

For a remediation method to gain a widespread use, it has to be considered economically feasible. The cost prices of some realized projects with stabilization for soil and harbour sediments are presented in Table 6.

The cost of soil stabilization with Fe-WTR comprises only transport of the amendment and soil mixing, which results in a low price compared to other soil stabilization methods presented in Table 6. Since most waterworks are distributed in relatively small units transport is often short if one wants to use Fe-WTR at a given site. For the small field scale experiment presented in Table 6 cost per m^3 will be likely to decrease when mixing more than 200 m^3 of soil.

A life cycle assessment, comparing landfilling and *in situ* stabilization, estimated a lower overall impact from soil stabilization mostly because transport of soil is omitted when treating soil *in situ* (Harbottle et al., 2007). When considering *in situ* stabilization it is important to include the costs of long term monitoring (Marques et al., 2011), which will add significantly to the total price of the remediation. However, at most contaminates sites monitoring is ongoing and after soil stabilization the existing monitoring scheme can be continued.

Table 6: Examples of cost for S/S and landfilling of soils and sediments, not including monitoring. Prices are not corrected for inflation.

Site/facility	Country	Type	Contaminants	Cost [dkk/m^3]
Hammarby Sjöstad, Stockholm[1]	Sweden	Harbour sediments, S/S, *in situ*	Hg	304-320
Nordsjö Hamn[1]	Finland	Harbour sediments, S/S, *ex situ*	TBT, PCB, metals	160
Kolding Harbour[2]	Denmark	Harbour sediments, S/S, *in situ*	Unknown	142
Range of 29 completed sites[3]	United States	S/S, both	Several	51-7706
Average of 27 completed sites[3]	United States	S/S, *in situ*	Several	1246
RSG 90, Copenhagen soil facility[4]	Denmark	Soil washing and *ex situ* landfilling Excl. excavation and transport	Heavy metals Conc. up to 10 x class 3[a]	641
RSG 90, Copenhagen soil facility[4]	Denmark	*Ex situ* landfilling Excl. excavation and transport	All, Class 3	119
Collstrop, Hillerød[5]	Denmark	Stabilization with WTR, *in situ*	As, Cr, Cu	300
As above with ZVI[5, 6]	Denmark	Stabilization with 1% ZVI, *in situ*	As, Cr, Cu	460

[1](Svedberg and Holm, 2007) [2](Jensen, 2012) [3](US EPA, 2002) [4](RGS 90, 2011) [5](Nielsen et al., II) [6]Assuming a cost of 10000 dkk/ton for ZVI [a]see Table 4 for criteria. To compare prices, some references have been recalculated to m^3 assuming a soil density of 1.6 ton/m^3.

5.5 Long-term stability of WTR amendment

The greatest obstacle for a widespread application of Fe-WTR is the uncertainty with regards to the long term containment of the contaminants. Adsorbed contaminants may be released through four different mechanisms:

- Drastic changes in soil pH
- Competing species, like phosphate and carbonate
- Transformation of ferrihydrite
- Reductive dissolution

Drastic pH changes are not likely to occur if the amended soil is left undisturbed, either *in situ* or *ex situ* in a landfill and no other amendments, e.g. lime ($CaCO_3$) which will increase pH, are added to the soil. Laboratory studies have shown, that up to 50% of adsorbed arsenic may desorb on the application of very high amounts of phosphorous fertilizer corresponding to 7500 mgP/kg soil (Sarkar et al., 2007b). The first and second release mechanism can therefore be avoided by limiting access to the soil. In any case, it is not recommended that other soil amendments such as lime, cement or phosphorous fertilizers are applied to the Fe-WTR amended soil.

As described in Sections 3.4 and 4.5 ferrihydrite is a metastable mineral, which undergoes recrystallization and may be the subject of iron reduction. Results presented in this thesis do not allow quantifying to which extent the transformation will influence leaching of contaminants from Fe-WTR amended soil and further research on the subject is called for.

Reductive dissolution is the likely cause of Fe release into the soil porewater in the unamended control experiment (Nielsen et al. II). However, a peak iron concentration of 500 µg/L during the months of July to November (Fig. 6) corresponds to a very small fraction of both the natural soil Fe and the Fe added as amendment. Solubilisation of iron is of course a concern when applying Fe-WTR as a soil amendment, as soluble iron will be transported with the soil and later ground water flow. Iron oxides may then slowly get depleted, but with the amount released in the field experiment, iron amendment of $5\%_{dw}$ Fe-WTR will not be depleted within hundreds of years. Most importantly this increase in dissolved iron was not observed for the amended plot treated with Fe-WTR.

Redox conditions may have been different in the plots, but no increased levels of iron or contaminants could be linked with water table fluctuations. Increased leaching of arsenic from amended soil during the wet season has been observed (Nielsen et al. I), making it not recommendable to use the stabilized soil for backfilling below a water table. In case of perched water tables as was the case of the Collstrop field site (Nielsen et al., I, II and III) drainage is recommended to avoid waterlogging and long periods of reducing conditions.

There is no doubt that under strongly reducing conditions stabilization with iron oxides is useless. Fe-WTR stabilization under mature landfill conditions is not feasible, as strongly reducing conditions will lead to reductive dissolution of the water treatment residues (Ghosh et al., 2006). Landfilling of stabilized soil must happen at controlled sites where the soil is not mixed with highly reactive carbon sources like municipal solid waste, as this will increase the potential for arsenic leaching (Jing et al., 2003).

6 Conclusions

In this PhD work I studied a novel technique of chemical soil stabilization at laboratory, pilot and full scale application using iron water treatment residues (Fe-WTR) to a Chromated Copper Arsenate (CCA) contaminated site. From the literature review presented in the thesis, as well as from the experimental work and field work presented in the papers, the following conclusions were drawn:

- Due to its chronic toxicity and because of its high mobility in soil and groundwater, arsenic often constitutes a threat to surface waters and drinking water resources downstream of former wood impregnation sites. The other chemicals used, copper and chromium, constitute a much lower threat. Chromium, which was used in its mobile and carcinogenic form Cr(VI) at the wood impregnation sites, is normally reduced to poorly soluble Cr(III) in the uppermost part of the soil due to the presence of organic matter. Furthermore, copper at the pH present at CCA sites is normally adsorbed in the uppermost organic rich soil, leaving arsenic as the mobile part of the contamination.

- A way to control exposure from the CCA sites is to chemically stabilize the soil reducing either solubility of the arsenic and/or limit hydraulic conductivity in the soil. The literature review showed that oxidized iron species can work as a sorbent for a number of metals and metalloids at both field and lab scale. A cheap and readily available iron oxide source in Denmark is Fe-WTR, due to natural conditions of the treated groundwater and the widespread number of water works. Similar conditions exist in a number of other countries as well.

- Fresh Fe-WTR act as a very efficient sorbent especially for arsenic and to a lesser extent copper and chromium as documented under field conditions and in laboratory batch experiments for arsenic and chromium. In the batch experiment 2 soils with different contaminant concentrations were amended with $5\%_{dw}$ Fe-WTR and As and Cr and leachate concentrations decreased by 98% and 93% respectively for the most contaminated soil.

- A small field experiment with 2.5%$_{dw}$ Fe-WTR decreased leachate concentrations of arsenic by two orders of magnitude from around 11,000-80,000 µg/L to a baseline below 100 µg/L in the two upper levels of porewater at 30 and 60 cm below surface and around 1000 µg/L in the lowest sampler. Some seasonal variation was observed, as As leaching increased from both the amended and unamended soil in the deepest level of porewater sampling and was linked to high precipitation rates resulting in a rising groundwater table and thereby possible iron reducing conditions.

- A full scale experiment was conducted at the Collstrop brownfield to stabilize 100 m^3 of contaminated soil. Soil and Fe-WTR mixing proved difficult in this first attempt with the chosen method and resulted in an inhomogeneous distribution of iron in the amended plot. With only 0.6 %$_{dw}$ Fe-WTR added dissolved concentration of As, Cr and Cu decreased significantly and seasonal release of contaminants, due to iron reduction, was not observed during one full year of monitoring.

- Ageing of ferrihydrite is a concern for the long-term use of Fe-WTR as soil amendment. In a natural soil environment, the transformation of ferrihydrite from the Fe-WTR was measured after 4 years and showed that about 60% of the ferrihydrite in Fe-WTR was transformed to a less ascorbate reducible iron fraction. Mineralogical characterization suggested the end product to be primarily goethite, a common iron mineral. Contaminants were equally associated with oxalate-extractable Fe and the more crystalline transformation product, which indicate, that increased leaching due to aging of ferrihydrite is not imminent. However, the batch experiment indicated that arsenic retention decreased slightly during 103 days, possibly due to ferrihydrite transformation.

- *Ex situ* soil amendment with Fe-WTR may find its use for lightly polluted soils for reuse in construction works. For the *ex situ* treatment of heavily contaminated soils, Fe-WTR may be used to control leaching of contaminants at landfills, but special care has to be given to the redox conditions, so that the soil is not landfilled in strongly reducing environments.

7 Perspectives

The need for alternative methods for the treatment of arsenic and heavy metal polluted soil calls for ongoing research as to find the most economically feasible and efficient technologies. As soil stabilization with Fe-WTR is a novel technology, improvements to the current methods applied in this thesis are needed in order to develop it for commercial use. Further investigations of the following points are suggested:

- As only a few different dosages of Fe-WTR have been tested and all tests have been performed with soil from the same site, conclusions on the optimal dosage of Fe-WTR for soil amendment cannot be made. **Dosage of Fe-WTR must be further studied in a systematic experiment** to investigate the influence from different **contaminant levels and soil matrices** with different structure, organic matter content and pH, which all may influence the sorption process.

- **Distribution of the amendment** at the current field experiment proved insufficient. This is seen as a technical rather than a scientific issue. Sufficient distribution may be obtained by optimizing the applied technique or choosing other equipment for soil mixing.

- If Fe-WTR is to be used for brownfield regeneration an assessment of the toxicity of Fe-WTR towards vegetation and other living organisms is crucial. Therefore **toxicity and other effects of applying of Fe-WTR to soil** have to be uncovered. This also includes **geotechnical stability of amended soil**, as adding a soil amendment may change the geotechnical properties of amended soil, possibly limiting future land-use.

- The use of a by-product may reduce installation costs, but how does Fe-WTR stabilization perform when compared to other remediation options during a life cycle assessment? Monitoring costs for stabilized sites will be substantial, so **economic and environmental impacts of the method have to be clarified and** will give insight to pros and cons compared to other soil stabilization and metal(loid) remediation methods in general.

During this PhD work questions, that require further research concerning the fate and transformation of ferrihydrite and other iron oxides in soil, have arisen. In order to fully explain the fate of Fe-WTR and ferrihydrite in soil environments following research is needed:

- Modeling or field studies is needed to predict the release of contaminants at various pH and redox conditions, in order to identify **controlling factors of contaminant release kinetics, when soils becomes flooded.** It is necessary to identify the threshold for contaminant release and estimate when that occurs in a flooded soil, if Fe-WTR is to be used as a soil amendment in general.

- Also the fate of contaminants associated with ferrihydrite as the ferrihydrite undergoes enevitable transformation to secondary iron phases is not fully understood. Long term studies of complete ferrihydrite transformation have so far only been carried out in uncontaminated *in vitro* studies and **final transformation product of ferrihydrite aged in soil environments** has still not been completely characterized. Quantification of the decrease in sorption capacity with time is crucial for the long term retention of contaminants by Fe-WTR stabilization.

Apart from technical and scientific questions, the method has perspectives that have not been touched upon in this PhD work and which may broaden the use of Fe-WTR as a soil amendment:

- Stabilization by Fe-WTR may work for other types of arsenic and heavy metal contamination than CCA from wood impregnation. A whole range of **other types of pollution sources** e.g. pesticides, mining activities and industrial manufacturing may be remediated by this method.

- If, as it seems from the full scale experiment presented in this thesis, the amendment of soil with Fe-WTR can improve vegetation cover, it does not only improve the esthetic value of the sites but may also make it possible to utilize the brownfields for **biomass production** e.g. for bioenergy or first generation biofuel. Also increased evapotranspiration from the contaminated site will decrease the amount of percolating water and thereby decrease leaching of contaminants to the groundwater. Before implementing this, uptake and transport of contaminants by the biomass has to be considered to avoid spreading of contaminants.

8 References

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9 Papers

I. Nielsen, S. S., L. R. Pedersen, P. Kjeldsen and R. Jakobsen (2011): **Amendment of arsenic and chromium polluted soil from wood preservation by iron residues from water treatment.** Chemosphere 84(4) p. 383-389

II. Nielsen, S. S., P. Kjeldsen and R. Jakobsen**: Field scale amendment of a wood impregnation site using iron water treatment residues** (submitted to Journal of Soils and Sediments)

III. Nielsen, S.S., P. Kjeldsen, H. C. B. Hansen and R. Jakobsen**: Transformation of natural ferrihydrite aged in As, Cr and Cu contaminated soil studied by reduction kinetics** (submitted to Applied Geochemistry)

In this online version of the thesis, the papers are not included but can be obtained from electronic article databases e.g. via www.orbit.dtu.dk or on request from:

DTU Environment
Technical University of Denmark
Miljoevej, Building 113
2800 Kgs. Lyngby
Denmark

reception@env.dtu.dk.

The Department of Environmental Engineering (DTU Environment) conducts science-based engineering research within four sections:
Water Resources Engineering, Urban Water Engineering,
Residual Resource Engineering and Environmental Chemistry & Microbiology.

The department dates back to 1865, when Ludvig August Colding, the founder of the department, gave the first lecture on sanitary engineering as response to the cholera epidemics in Copenhagen in the late 1800s.

DTU Environment
Department of Environmental Engineering
Technical University of Denmark

Miljoevej, building 113
2800 Kgs. Lyngby
Denmark

Phone: +45 4525 1600
Fax: +45 4593 2850
e-mail: reception@env.dtu.dk
www.env.dtu.dk